

Abstract:

Introduction:

Stromatolites are a calciferous formation commonly thought to be created by cyanobacteria, either through the trapping and binding of sediment, or through metabolically-induced precipitation. Stromatolites are currently thought to be one of the earliest forms of life on Earth, dating back to approximately 3.5 billion years ago. However, stromatolites' form diversity in the fossil record decreases significantly for an extended period of time beginning slightly before the Precambrian-Cambrian boundary, only to resurface first after the Permian-Triassic (PT) extinction, and then again after the Triassic-Jurassic (TJ) extinction (two of the biggest mass extinctions in Earth's history). This original decrease in form diversity is attributed to many factors: including changing ocean chemistry, algal evolution and the resulting competition for sea-floor space, and exposure to grazers (Grotzinger 1999). The main theory for the resurface of these post-extinction stromatolites is the lack of competition from benthic corals as well as the lack of predation from grazing fauna (Bottjer 2011).

These stromatolites were chosen for examination as they straddle two of the largest extinctions in the history of planet Earth. The PT Mass Extinction is thought to have been caused by increases in CO₂ gas in the atmosphere from erupting volcanoes in Siberia. These increases in CO₂ would have led to increases in temperature and decreases in oxygen solubility in shallow water environments. The TJ Mass Extinction is also thought to be associated with volcanic activity, but this volcanic activity took place at the Central Atlantic Magmatic Province. The new crust formed from this volcanic activity caused the spread of the Earth's crust, which initiated the breakup of Pangaea. This increase in volcanic activity corresponds to

an increase in atmospheric CO₂ levels as well as an increase in temperature of approximately 3-4°C. Thus stromatolites from these eras were chosen as they formed under similar conditions, in terms of atmospheric and temperature changes, to what is occurring in our present-day biosphere. These stromatolites also provide the distinct advantage of being relatively newer stromatolites, in comparison to Achaean and Proterozoic forms, and are less subject to alterations or to the diagenesis of their carbonate forms.

Despite their geobiologic importance, the mechanisms that govern stromatolite formation are not well understood. I plan on using stromatolites from these post-extinction eras in order to better understand the environment of their formation, specifically temperature and pH, by utilizing the method of multiply substituted isotopologues of CO₂ (the carbonate “clumped” isotope paleothermometer). Using this data, in combination with the most recent projections for climate change (change in atmospheric CO₂, temperature, and ocean acidity), I hope to determine if it is possible for stromatolites to reappear in the modern ocean due to rising water temperature and falling pH.

Using the CHEMIN data obtained from the Planetary Data System (PDS), I will construct a climate model of Mars based off the mineralogical data obtained *in situ*. This model will be compared to the climate data obtained from the stromatolite samples to determine if conditions favoring stromatolite formation were present within the history of Mars.

The PT and TJ extinction boundary stromatolites will be analyzed using clumped isotope thermometry. In clumped isotope thermometry, the mass spectrometer measures the abundance of heavy isotopes of CO₂ and compares them to an absolute reference scale. By comparison to this reference scale the temperature of formation for the carbonate samples can be calculated as

more heavy-isotopes clump at lower temperatures. The most common isotope of carbon dioxide is $^{12}\text{C}^{16}\text{O}^{16}\text{O}$, whereas only a small fraction of CO_2 forms the heavier isotopes of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$. Measuring the abundance of such heavy isotopes can allow for the calculation of the temperature of formation within a 1-3°C certainty (Huntington 2009).

Method:

Stromatolites will be obtained from the appropriate extinctions boundaries: the PT stromatolites will be the same stromatolites studied by Matta and Bottjer (2011) and the TJ stromatolites were obtained from the UK and are known as Cotham Marble. Due to the uneven distribution of the fossil record, some of these stromatolites are from places not easily accessible to researchers. These stromatolites will be obtained from various other stromatolite researchers (David Bottjer, Carlie Pietsch (USC) for PT – Sarah Greene (University of Bristol) and Yadira Ibarra (USC) for TJ).

Once the stromatolites have been obtained they will be drilled. This drilling is to obtain a fine powder that can be weighed out and run on a Thermo-Finnigan MAT 253 dual-inlet gas-source Isotope Ratio Mass Spectrometer. The stromatolites will be drilled at the best location possible to obtain high amounts of un-altered, primary calcium carbonate. After the stromatolites have been drilled, the powder is collected and stored in a desiccator until the samples will be run on the mass spectrometer.

One sample of stromatolite is approximately 8 mg of carbonate powder. This amount will be weighed out, and placed in silver capsules for delivery into the mass spectrometer. The silver capsules containing samples will be individually dropped into a bath of heated phosphoric acid via a Costech autosampler. This acid bath will break down the carbonate into carbon

dioxide which can be analyzed on the mass spectrometer. This carbon dioxide is then purified through a series of cold traps, both an ethanol and liquid nitrogen trap, which will freeze any impurities in the gas sample and evacuate them through a vacuum. In between traps the gas sample is run through a gas chromatograph (GC) which cools the sample to remove organic compounds. Once organic matter is removed, the gas is again purified before being transferred to the mass spectrometer. The mass spectrometer will return a bulk isotopic reading which is then plotted against a line derived from bulk isotopic readings at 1000° C (a temperature with no clumping) and room temperature (a temperature with a standardized set of clumping). Based off of this line, the temperature of formation is known for the sample.

A climate model for Mars will be constructed using the mineralogical data obtained *in situ* from Mars by the Mars Rovers. Using known temperatures and conditions of formation for each mineral the climate of Mars on a geological time scale can be deduced, after adjusting these conditions of formation to the Martian atmosphere. This extrapolated data will be compared to the data obtained from isotopic analysis of the stromatolites to see if similar temperature ranges existed on Mars to allow for stromatolite formation.

The temperature and pH data obtained from isotopic analysis of the stromatolites will be taken one step further: it will be compared to projected climate models for the Earth. Current climate models show a general increase in temperature and decrease in pH of the ocean, mostly attributed to anthropogenic increases in greenhouse gases, especially CO₂ which is also causing the drop in oceanic pH. After comparing these data sets, it is possible to predict a potential resurgence in stromatolite form diversity, or whether resurgence is unexpected as a result of non-correlating trends.

Timeline:

Month and Year	Progress Towards Completion
March 2014	Proposal approval
April 2014	gathering of samples from different sites (some samples have already been obtained) running samples on mass spectrometer, recording of data
May 2014	gathering of samples from different sites (some samples have already been obtained) running samples on mass spectrometer, recording of data
June 2014	running samples on mass spectrometer, recording of data organizing and analyzing data
July thru September 2014	Analyzing data and writing paper
October thru November 2014	Possible presentation of paper at professional meeting Writing of final draft of paper
December 2014 thru February 2015	Writing of final draft of paper
March 2015	Writing of final draft of paper Possible conference presentation
April 2015	Final paper due